

# Semiclassical theory of vibrational energy relaxation

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(November 12, 1997)

## Abstract

A theory of vibrational energy relaxation based on a semiclassical treatment of the quantum master equation is presented. Using new results on the semiclassical expansion of dipole matrix elements, we show that in the classical limit the master equation reduces to the Zwanzig energy diffusion equation. The leading quantum corrections are determined and discussed for the harmonic and Morse potentials.

## I. INTRODUCTION

Vibrational energy relaxation (VER) is of fundamental importance for many chemical reactions in solution<sup>1,2</sup>. VER studies in molecules like I<sub>2</sub>, HgI, O<sub>2</sub>, and N<sub>2</sub> in various solvents by means of pulsed laser techniques cover a range of relaxation times from picoseconds to seconds<sup>2</sup>. A detailed theoretical description is often complicated by the fact that various energy relaxation processes contribute. While in the high frequency regime a quantum mechanical treatment, e. g., on the basis of the isolated binary collision model is natural, the low frequency regime has for the most part been treated in terms of classical theories such as the Landau-Teller model, the generalized Langevin equation, or by molecular dynamics<sup>3–5</sup>. These approaches are justified for high temperatures and heavier molecules.

However, in some of the above mentioned molecules in solution as well as for adsorbates on surfaces, molecules in cryogenic matrices, or molecular crystals, purely classical theories are not sufficient and quantum effects cannot be disregarded. This is also due to the fact that experiments have to be performed at low temperatures where only few vibrational levels are occupied. For these systems, VER was mostly treated on the basis of Fermi’s golden rule and the quantum master equation<sup>6,7</sup>.

One of the questions arising in this context is the connection between the quantum mechanical theory of VER and classical energy relaxation. To address this problem, we give here a semiclassical analysis of the quantum master equation. The Zwanzig energy diffusion equation<sup>4</sup> is recovered in the classical limit and the dominant quantum corrections are determined explicitly.

The paper is organized as follows. In section II we introduce the microscopic model which is a nonlinear oscillator coupled to a bath of harmonic oscillators. This model is known to lead in the classical limit to the generalized Langevin equation. Molecular dynamics simulation suggest that the model can also be used for rather complicated relaxation processes, such as e.g., a binary molecule in a Lennard-Jones fluid, if the parameters of the harmonic oscillator bath are chosen appropriately<sup>5</sup>. We briefly discuss the classical limit of the model,

and its weak-coupling limit, which leads to the Zwanzig energy diffusion equation. Further, the fully quantum mechanical treatment of VER on the basis of a master equation is given.

Section III is devoted to the semiclassical expansion of the master equation. This requires, apart from known expansions of wave functions and energy levels, explicit results on semiclassical dipole matrix elements. On the basis of these results we then show that the master equation reduces to the classical energy diffusion equation in the limit  $\hbar \rightarrow 0$ , and determine the leading quantum corrections. Section IV contains explicit results for the cases of the harmonic and Morse potentials, and in section V we present our conclusions.

## II. THE MODEL AND FORMULATION OF THE PROBLEM

Vibrational motion of molecules can be modeled as the motion of a particle in an anharmonic potential well  $V(q)$ . To account for dissipation we couple the particle to a bath of harmonic oscillators<sup>8</sup>. Of course, the harmonic oscillator bath is a crude simplification of the real interaction of molecular vibrations with the solvent. However, inasmuch as the back-action of the solvent can be treated within linear response theory, the bath can be modeled in terms of effective bath oscillators. In fact, this simple model describes the classical dynamics of a binary molecule in a Lennard-Jones fluid quite accurately<sup>5</sup>. For the problem of energy relaxation we expect the harmonic oscillator bath to be a reasonable starting point. With these premises, the Hamiltonian  $H$  is composed of the oscillator part

$$H_S = \frac{p^2}{2M} + V(q), \quad (1)$$

the bath Hamiltonian

$$H_B = \sum_{n=1}^N \frac{p_n^2}{2m_n} + \frac{m_n}{2} \omega_n^2 x_n^2, \quad (2)$$

and an interaction part

$$H_{SB} = -q \sum_{n=1}^N c_n x_n + q^2 \sum_{n=1}^N \frac{c_n^2}{2m_n \omega_n^2}. \quad (3)$$

It is well known<sup>8</sup> that the associated classical equation of motion is the generalized Langevin equation

$$M\ddot{q}(t) + V'(q(t)) + M \int_0^t ds \gamma(t-s) \dot{q}(s) = \xi(t) \quad (4)$$

where the prime denotes differentiation with respect to the argument, and

$$\gamma(t) = \frac{1}{M} \sum_{n=1}^N \frac{c_n^2}{m_n \omega_n^2} \cos(\omega_n t) \quad (5)$$

is the damping kernel. Finally,  $\xi(t)$  is a stochastic force having the properties

$$\langle \xi(t) \rangle = 0 \quad (6)$$

and

$$\langle \xi(t) \xi(0) \rangle = M k_B T \gamma(t). \quad (7)$$

We will be interested in the motion at weak damping. When  $\omega_0$  is the frequency of small undamped oscillations about the minimum of the potential well, a typical damping strength is given by

$$\gamma_c = \int_0^\infty dt \gamma(t) \cos(\omega_0 t). \quad (8)$$

Further, we may introduce a typical memory delay time

$$\tau_c = \frac{\int_0^\infty dt t \gamma(t) \cos(\omega_0 t)}{\int_0^\infty dt \gamma(t) \cos(\omega_0 t)}. \quad (9)$$

The region of damping parameters examined in this article is then characterized by

$$\gamma_c \ll \omega_0, 1/\tau_c. \quad (10)$$

Let us briefly recall the *classical treatment* of this weak damping limit. Under the conditions stated, the unperturbed energy

$$E = \frac{M}{2} \dot{q}^2 + V(q) \quad (11)$$

of the particle will be an almost conserved quantity, and it is advantageous to rewrite the classical Langevin equation in terms of energy and phase variables.

The unperturbed trajectory  $q(E, t)$  of energy  $E$  satisfying

$$M\ddot{q} + V'(q) = 0 \quad (12)$$

may be written as a Fourier series

$$q(E, t) = \sum_{l=-\infty}^{\infty} Q_l(E) e^{il\Phi(t)} \quad (13)$$

where

$$\Phi(t) = \omega(E)t. \quad (14)$$

Here  $2\pi/\omega(E)$  is the oscillation period of a trajectory of energy  $E$  in the potential well. The phase will be chosen such that for  $\Phi = 0$  the trajectory is at a turning point. Then the Fourier coefficients are real and satisfy

$$Q_{-l}(E) = Q_l(E). \quad (15)$$

Now, relation (13) and

$$\dot{q}(E, t) = \sum_{l=-\infty}^{\infty} il\omega(E)Q_l(E)e^{il\Phi(t)} \quad (16)$$

define a mapping from the variables  $q, \dot{q}$  to the variables  $E, \Phi$ . By means of this transformation, the Langevin equation may be written in terms of energy and phase<sup>4,9,10</sup>. These transformed equations may be solved perturbatively to second order in the coupling to the bath. Within the time window

$$1/\omega_0, \tau_c \ll t \ll 1/\gamma_c \quad (17)$$

the solution can be matched with the solution of a Fokker-Planck equation for the energy and phase distribution function<sup>10</sup>. The structure of the resulting Fokker-Planck process allows one to average over the phase variable yielding the one-dimensional Fokker-Planck equation

$$\dot{P}(E) = \frac{\partial}{\partial E} \Lambda(E) \left( 1 + k_B T \frac{\partial}{\partial E} \right) \frac{\omega(E)}{2\pi} P(E). \quad (18)$$

where

$$\Lambda(E) = 2\pi M \omega(E) \sum_{l=-\infty}^{\infty} l^2 Q_l^2(E) \hat{\gamma}(il\omega(E)) \quad (19)$$

is the energy relaxation coefficient. Here

$$\hat{\gamma}(z) = \int_0^{\infty} dt e^{-zt} \gamma(t) \quad (20)$$

is the Laplace transform of the damping kernel. Eq. (18) is the energy diffusion equation first derived by Zwanzig<sup>4</sup>.

We now turn to the problem of energy relaxation in a weakly damped *quantum system*. Introducing the energy eigenstates of the unperturbed system

$$H_S |n\rangle = E_n |n\rangle, \quad n = 0, 1, 2, \dots \quad (21)$$

we start from the Pauli master equation

$$\dot{p}_n(t) = \sum_{m=0}^{\infty} [W_{n,m} p_m(t) - W_{m,n} p_n(t)] \quad (22)$$

where  $p_n(t)$  is the probability to find the system in state  $n$  at time  $t$ . The transition rate from state  $m$  to  $n$  may be calculated by Fermi's golden rule

$$W_{n,m} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \text{Tr}_B [\langle n | H_{SB}(t) | m \rangle \langle m | H_{SB} | n \rangle \rho_B^{\text{eq}}]. \quad (23)$$

Here  $\text{Tr}_B$  denotes the trace over the bath states,  $\rho_B^{\text{eq}} = e^{-\beta H_B} / \text{Tr}_B [e^{-\beta H_B}]$  is the equilibrium bath density matrix, and  $H_{SB}(t) = e^{i(H_S + H_B)t/\hbar} H_{SB} e^{-i(H_S + H_B)t/\hbar}$ . Using Eq. (3), we obtain

$$W_{n,m} = \frac{1}{\hbar^2} \langle n | q | m \rangle^2 \sum_{k,l=1}^N c_k c_l \int_{-\infty}^{\infty} dt e^{i(E_n - E_m)t/\hbar} \text{Tr}_B [x_k(t) x_l \rho_B^{\text{eq}}]. \quad (24)$$

In the weak damping limit considered here, the so-called counter-term, that is the second term of  $H_{SB}$  in Eq. (3), may be disregarded. The master equation (22) is appropriate for weak damping satisfying condition (10). In addition, for the quantum system a further

frequency scale set by the lowest Matsubara frequency  $\nu \equiv 2\pi k_B T/\hbar$  becomes relevant. As can be seen from the derivation of the Pauli master equation, bath correlation functions are assumed to decay on a time scale much shorter than  $1/\gamma_c$  (see for instance Ref. 11). For low temperatures where  $\nu < 1/\tau_c$  bath correlations decay on the time scale  $1/\nu$ . Hence, in addition to Eq. (10) we have to require

$$\gamma_c \ll \nu \quad (25)$$

which is, however, usually obeyed for systems of relevance in chemical physics.

Due to the linearity of the bath, the transition rate may be evaluated exactly yielding

$$W_{n,m} = \frac{1}{\hbar^2} \langle n|q|m \rangle^2 D(E_n - E_m). \quad (26)$$

Here

$$D(E) = 2ME\bar{n}(E)\text{Re } \hat{\gamma}(i|E|/\hbar) \quad (27)$$

is an effective, occupation weighted spectral density of the bath with the Bose occupation function

$$\bar{n}(E) = \frac{1}{e^{\beta E} - 1}. \quad (28)$$

Note that the coupling to the bath is completely described in terms of the Laplace transform of the damping kernel. Since the detailed balance condition

$$W_{m,n} = e^{\beta(E_n - E_m)} W_{n,m} \quad (29)$$

is clearly obeyed, it is readily seen that Eq. (22) has the stationary solution

$$p_n = \frac{1}{Z} e^{-\beta E_n} \quad (30)$$

where

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} \quad (31)$$

is the quantum mechanical partition function.

### III. SEMICLASSICAL EXPANSION OF THE PAULI MASTER EQUATION

We now want to regain the Zwanzig energy diffusion equation from the Pauli master equation and determine the leading quantum corrections. The results of this somewhat lengthy calculation are summarized at the beginning of section IV. We start by introducing the probability distribution function

$$P(E) := \sum_{n=0}^{\infty} \delta(E - E_n) p_n \quad (32)$$

by means of which expectation values are simply calculated as

$$\langle f(E) \rangle = \int_{-\infty}^{\infty} dE P(E) f(E) \quad (33)$$

for arbitrary  $f(E)$ . In terms of the function  $N(E)$  which counts the number of energy levels below energy  $E$

$$N(E) = \sum_{n=0}^{\infty} \Theta(E - E_n), \quad (34)$$

the probability  $P(E)$  can be written

$$P(E) = \rho(E) p_{N(E)} \quad (35)$$

where

$$\rho(E) = \frac{\partial N(E)}{\partial E} = \sum_{n=0}^{\infty} \delta(E - E_n) \quad (36)$$

is the level density. Now, combining Eqs. (22) and (32) we find

$$\begin{aligned} \dot{P}(E) &= \sum_{n,m=0}^{\infty} [\delta(E - E_m) - \delta(E - E_n)] W_{m,n} p_n \\ &= \sum_{n=0}^{\infty} \sum_{l=-n}^{\infty} [\delta(E - E_{n+l}) - \delta(E - E_n)] W_{n+l,n} p_n. \end{aligned} \quad (37)$$

This equation will be evaluated in the semiclassical limit in the sequel.



### A. Semiclassical energies

To proceed we need to determine the semiclassical energy eigenvalues and dipole matrix elements. We start from the semiclassical (WKB) expansion of the wave function

$$\langle q|E\rangle = \sqrt{\frac{2M}{\pi C(E)}} e^{iS(E,q)/\hbar} \quad (38)$$

where  $C(E)$  is a normalization factor. Inserting this ansatz into the Schrödinger equation and expanding in powers of  $\hbar$ , one arrives at the usual eikonal expansion

$$S(E, q) = S_0(E, q) - i\hbar S_1(E, q) - \hbar^2 S_2(E, q) + i\hbar^3 S_3(E, q) + \dots \quad (39)$$

where the  $S_i(E, q)$  can be calculated recursively with the result<sup>12</sup>

$$\begin{aligned} \frac{\partial}{\partial q} S_0(E, q) &= p(E, q) = \sqrt{2M[E - V(q)]}, \\ \frac{\partial}{\partial q} S_1(E, q) &= -\frac{1}{2} \frac{\partial}{\partial q} \ln p(E, q), \\ \frac{\partial}{\partial q} S_2(E, q) &= \frac{1}{4p(E, q)^2} \frac{\partial^2}{\partial q^2} p(E, q) - \frac{3}{8p(E, q)^3} \left[ \frac{\partial}{\partial q} p(E, q) \right]^2, \\ \frac{\partial}{\partial q} S_3(E, q) &= \frac{1}{2} \frac{\partial}{\partial q} \frac{1}{p(E, q)} \frac{\partial}{\partial q} S_2(E, q). \end{aligned} \quad (40)$$

To second order in  $\hbar$  the wave function is then given by

$$\begin{aligned} \langle q|E\rangle^{(\pm)} &= \sqrt{\frac{2M}{\pi C(E)p(E, q)}} \exp \left\{ \pm \frac{i}{\hbar} S_0(E, q) \pm \frac{\hbar}{i} S_2(E, q) \right. \\ &\quad \left. - \frac{\hbar^2}{2p(E, q)} \frac{\partial S_2(E, q)}{\partial q} + \mathcal{O}(\hbar^3) \right\}. \end{aligned} \quad (41)$$

The solution to the two turning point problem we are facing here is a linear combination of these right and left traveling waves. Details of the analytic structure of these functions are discussed in the literature<sup>12</sup>. Here we only mention that the quantization condition is obtained as

$$\frac{i}{\hbar} \oint dq \frac{\partial S(E, q)}{\partial q} = 2\pi i n, \quad n = 0, 1, 2, \dots \quad (42)$$

by requiring the single-valuedness of the wave function. The integration contour is chosen to enclose the two turning points at energy  $E$ . Defining the function

$$N_{\text{sc}}(E) := \frac{1}{2\pi\hbar} \oint dq \frac{\partial S(E, q)}{\partial q}, \quad (43)$$

this quantization condition may be written as

$$N_{\text{sc}}(E) = n, \quad n = 0, 1, 2, \dots \quad (44)$$

The semiclassical energy eigenvalues  $E_{\text{sc}}(n)$  ( $n = 0, 1, 2, \dots$ ) are then obtained by inverting Eq. (44). Now, the semiclassical expansion of Eq. (43) gives<sup>12</sup>

$$N_{\text{sc}}(E) = \frac{1}{\hbar} J_0(E) - \frac{1}{2} - \hbar J_2(E) + \mathcal{O}(\hbar^3) \quad (45)$$

where

$$J_{2k}(E) = \frac{1}{2\pi} \oint dq \frac{\partial S_{2k}(E, q)}{\partial q}. \quad (46)$$

Here  $J_0(E)$  is the action variable with the property

$$\frac{\partial J_0(E)}{\partial E} = \frac{1}{\omega(E)}. \quad (47)$$

Truncation of the series (45) at order  $\hbar$  reproduces the Bohr-Sommerfeld quantization condition. Note that it is necessary to distinguish the semiclassical quantity  $N_{\text{sc}}(E)$  from the exact  $N(E)$  which is a staircase function. For potentials where the series expansion (45) terminates at some finite order,  $N_{\text{sc}}(E)$  smoothly interpolates between the sharp steps of  $N(E)$ . Similarly, the exact quantum mechanical density  $\rho(E)$  has to be distinguished from the smooth semiclassical level density

$$\rho_{\text{sc}}(E) := \frac{\partial N_{\text{sc}}(E)}{\partial E} = \frac{1}{\hbar\omega(E)} - \hbar J_2'(E) + \mathcal{O}(\hbar^3). \quad (48)$$

Accordingly, we define a generalized oscillation frequency containing quantum corrections by

$$\Omega(E) := \frac{1}{\hbar\rho_{\text{sc}}(E)} = \omega(E) + \hbar^2 J_2'(E)\omega(E)^2 + \mathcal{O}(\hbar^4). \quad (49)$$

Another quantity useful below is the energy difference between nearby levels. Defining

$$\hbar A_l(E) := E_{\text{sc}}(N_{\text{sc}}(E) + l) - E, \quad (50)$$

we find with the help of Eq. (45)

$$\hbar A_l(E) = \hbar A_l^{(1)}(E) + \frac{\hbar^2}{2} A_l^{(2)}(E) + \frac{\hbar^3}{3!} A_l^{(3)}(E) + \frac{\hbar^4}{4!} A_l^{(4)}(E) + \mathcal{O}(\hbar^5), \quad (51)$$

where

$$\begin{aligned} A_l^{(1)} &= l\omega, \\ A_l^{(2)} &= \frac{l^2}{2} [\omega^2]', \\ A_l^{(3)} &= 6l\omega^2 J_2' + \frac{l^3}{2} \omega [\omega^2]'', \\ A_l^{(4)} &= 12l^2 [\omega^3 J_2']' + \frac{l^4}{2} \omega \left\{ \omega [\omega^2]'' \right\}'. \end{aligned} \quad (52)$$

Here we have suppressed the explicit energy dependence for clarity.

## B. Semiclassical matrix elements

As a first step to a calculation of semiclassical matrix elements the normalization factor  $C(E)$  needs to be determined. Extending previous work on semiclassical matrix elements<sup>13</sup>, one finds to second order in  $\hbar$

$$C(E) \approx \frac{M}{2\pi} \oint \frac{dq}{p(E, q)} \left[ 1 - \hbar^2 \frac{1}{p(E, q)} \frac{\partial S_2(E, q)}{\partial q} \right] = \frac{1}{\omega(E)} + \hbar^2 C^{(2)}(E) \quad (53)$$

where the last equality defines  $C^{(2)}(E)$ . Below we will need semiclassical expressions for the dipole matrix element

$$Q_l(E) := \langle E + \hbar A_l(E) | q | E \rangle. \quad (54)$$

It is, however, more convenient to evaluate the momentum matrix element

$$P_l(E) := \langle E + \hbar A_l(E) | p | E \rangle \quad (55)$$

from which the dipole matrix element can be obtained by means of the relation

$$P_l(E) = iMA_l(E)Q_l(E) \quad (56)$$

which is a consequence of  $[H, q] = \hbar p/iM$ . Combining Eqs. (54), (55), (56), and (41) one finds along these lines

$$\begin{aligned} Q_l(E) &= \frac{1}{iMA_l(E)} \int_{-\infty}^{\infty} dq \langle E + \hbar A_l(E) | q \rangle \frac{\hbar}{i} \frac{\partial}{\partial q} \langle q | E \rangle \\ &\approx \frac{1}{2\pi i A_l(E)} \oint dq \left[ p(E, q) + \frac{\hbar}{2i} \frac{1}{p(E, q)} \frac{\partial p(E, q)}{\partial q} - \hbar^2 \frac{\partial S_2(E, q)}{\partial q} \right] \\ &\quad \times \frac{\exp\left(\frac{i}{\hbar} \left\{ S_0(E, q) - S_0(E + \hbar A_l(E), q) - \hbar^2 [S_2(E, q) - S_2(E + \hbar A_l(E), q)] \right\}\right)}{\sqrt{C(E)p(E, q)C(E + \hbar A_l(E))p(E + \hbar A_l(E), q)}}. \end{aligned} \quad (57)$$

A systematic expansion in terms of  $\hbar$  then leads to

$$Q_l(E) = Q_l^{(0)}(E) + \hbar Q_l^{(1)}(E) + \frac{1}{2}\hbar^2 Q_l^{(2)}(E) + \frac{1}{6}\hbar^3 Q_l^{(3)}(E) + \mathcal{O}(\hbar^4) \quad (58)$$

where the zeroth order term is given by

$$Q_l^{(0)}(E) = \frac{1}{2\pi i l} \oint dq \exp[-il\omega(E)t(E, q)]. \quad (59)$$

Here we have introduced the time

$$t(E, q) := \frac{\partial S_0(E, q)}{\partial E} \quad (60)$$

spent by a particle of energy  $E$  on its way from the turning point to  $q$ . Transforming the integration variable and integrating by parts, it is seen that

$$Q_l^{(0)}(E) = \frac{\omega(E)}{2\pi} \int_0^{2\pi/\omega(E)} dt q(E, t) e^{-il\omega(E)t} \quad (61)$$

is just the Fourier coefficient of the classical trajectory introduced in Eq. (13). The first order correction is completely determined by the zeroth order term by means of

$$Q_l^{(1)}(E) = \frac{l\omega(E)}{2} [Q_l^{(0)}]'(E), \quad (62)$$

and the second order term is given by

$$\begin{aligned}
Q_l^{(2)}(E) = & \frac{l^2 \omega(E)}{4} [\omega Q_l^{(0)}]''(E) - \frac{l^2}{24} [\omega^2]''(E) Q_l^{(0)}(E) \\
& - 2 [J_2'(E) + C^{(2)}(E)] \omega(E) Q_l^{(0)}(E) \\
& + \frac{\omega(E)}{2\pi} \oint dq e^{-il\omega(E)t(E,q)} \left( 2 \frac{\partial}{\partial E} S_2(E, q) - \frac{2i}{l\omega(E)p(E, q)} \frac{\partial}{\partial q} S_2(E, q) \right. \\
& \quad \left. - 2\omega(E)t(E, q) J_2'(E) - \frac{7il\omega(E)M^2}{12p(E, q)^4} \right. \\
& \quad \left. - \frac{l^2}{12} \left\{ \omega(E)^2 \frac{\partial^2}{\partial E^2} t(E, q) + [\omega(E)\omega''(E) - 2\omega'(E)^2] t(E, q) \right\} \right).
\end{aligned} \tag{63}$$

In deriving Eq. (63) we have made repeated use of partial integrations. Note that the third order coefficient  $Q_l^{(3)}(E)$ , which is also needed in the sequel, is completely determined by  $Q_l^{(0)}(E)$  and  $Q_l^{(2)}(E)$ . As a consequence of the symmetry relation

$$\langle n|q|m \rangle = \langle m|q|n \rangle, \tag{64}$$

or, equivalently,

$$Q_l(E) = Q_{-l}(E + \hbar A_l(E)), \tag{65}$$

one finds with the help of Eqs. (51) and (45)

$$Q_l^{(3)} = \omega \left( \frac{3l}{2} [Q_l^{(2)}]' - 3l\omega J_2' [Q_l^{(0)}]' + \frac{l^3}{8} \left\{ [\omega^2]' [Q_l^{(0)}]'\right\}' - \frac{l^3}{4} \left\{ \omega^2 [Q_l^{(0)}]'\right\}'' \right). \tag{66}$$

This way we have expressed the quantum corrections to the dipole matrix element up to order  $\hbar^3$  by purely classical quantities.

For the semiclassical expansion of the master equation we need the squared matrix element

$$B_l(E) := \langle E + \hbar A_l(E) | q | E \rangle^2. \tag{67}$$

From the above results, its semiclassical expansion is given by

$$B_l(E) = B_l^{(0)}(E) + \hbar B_l^{(1)}(E) + \frac{\hbar^2}{2} B_l^{(2)}(E) + \frac{\hbar^3}{6} B_l^{(3)}(E) + \mathcal{O}(\hbar^4) \tag{68}$$

where

$$\begin{aligned}
B_l^{(0)} &= [Q_l^{(0)}]^2, \\
B_l^{(1)} &= \frac{l}{2}\omega [B_l^{(0)}]', \\
B_l^{(2)} &= \frac{l^2}{2}\omega^2 \left\{ [Q_l^{(0)}]'\right\}^2 + 2Q_l^{(0)}Q_l^{(2)}, \\
B_l^{(3)} &= \left\{ -\frac{l^3}{8}\omega [\omega^2]'' + 3l\omega^2 J_2' \right\} [B_l^{(0)}]' - \frac{l^3}{4} \left\{ \omega^3 [B_l^{(0)}]'' \right\}' + \frac{3l}{2}\omega [B_l^{(2)}]',
\end{aligned} \tag{69}$$

where we have again suppressed the explicit energy dependence.

### C. Semiclassical expansion of the probability

Let us now assume that there is a continuous function  $p_{\text{sc}}(x)$  which interpolates between the discrete values of  $p_n$  such that

$$p_{\text{sc}}(n) = p_n, \quad \text{for } n \text{ integer}, \tag{70}$$

as it is the case for the stationary solution (30) of Eq. (22). The probability (32) can now be written as

$$P(E) = \sum_{n=0}^{\infty} \delta(E - E_{\text{sc}}(n)) p_{\text{sc}}(n) = P_{\text{sc}}(E) \sum_{n=0}^{\infty} \delta(N_{\text{sc}}(E) - n), \tag{71}$$

where we have introduced

$$P_{\text{sc}}(E) = \rho_{\text{sc}}(E) p_{\text{sc}}(N_{\text{sc}}(E)), \tag{72}$$

and have made use of Eq. (45) and the fact that

$$\delta(E - E_{\text{sc}}(n)) = \rho_{\text{sc}}(E) \delta(N_{\text{sc}}(E) - n), \tag{73}$$

which is a version of the well-known relation

$$\delta(x) = |f'(x_0)| \delta(f(x)) \tag{74}$$

holding for functions  $f(x)$  with a single zero  $x_0$ . Now, the semiclassical expansion of  $P(E)$  can be obtained in the following way. With the help of the identity

$$\sum_{n=0}^{\infty} \delta(x-n) = \delta(x) + e^{-\frac{\partial}{\partial x}} \sum_{n=0}^{\infty} \delta(x-n) \quad (75)$$

we can write formally

$$\sum_{n=0}^{\infty} \delta(x-n) = \frac{\frac{1}{2} \frac{\partial}{\partial x}}{\sinh(\frac{1}{2} \frac{\partial}{\partial x})} \Theta(x + \frac{1}{2}). \quad (76)$$

Here the rhs is merely an abbreviation for the series

$$\frac{x}{\sinh(x)} = \sum_{n=0}^{\infty} \frac{2-2^{2n}}{(2n)!} B_{2n} x^{2n} = 1 - \frac{1}{6} x^2 + \frac{7}{360} x^4 + \dots \quad (77)$$

where the  $B_n$  are Bernoulli numbers. Now, in view of

$$\frac{\partial}{\partial N_{\text{sc}}} = \frac{\partial E}{\partial N_{\text{sc}}} \frac{\partial}{\partial E} \quad (78)$$

we have

$$\begin{aligned} \frac{\rho(E)}{\rho_{\text{sc}}(E)} &= \sum_{n=0}^{\infty} \delta(N_{\text{sc}}(E) - n) = \frac{\frac{1}{2\rho_{\text{sc}}(E)} \frac{\partial}{\partial E}}{\sinh(\frac{1}{2\rho_{\text{sc}}(E)} \frac{\partial}{\partial E})} \Theta(N_{\text{sc}}(E) + \frac{1}{2}) \\ &= \frac{\frac{\hbar\Omega(E)}{2} \frac{\partial}{\partial E}}{\sinh(\frac{\hbar\Omega(E)}{2} \frac{\partial}{\partial E})} \Theta(N_{\text{sc}}(E) + \frac{1}{2}). \end{aligned} \quad (79)$$

From Eq. (45) we find

$$\Theta(N_{\text{sc}}(E) + \frac{1}{2}) = \Theta(E) - \hbar^2 \omega(0) J_2(0) \delta(E) + \mathcal{O}(\hbar^3), \quad (80)$$

where we have used the fact that  $J_0(0) = 0$ . This combines with Eqs. (79) and (48) to yield the semiclassical expansion

$$\frac{\rho(E)}{\rho_{\text{sc}}(E)} = \Theta(E) - \frac{\hbar^2}{24} \omega(E) \omega(0) \delta'(E) - \hbar^2 \omega(0) J_2(0) \delta(E) + \mathcal{O}(\hbar^4). \quad (81)$$

Hence, from Eq. (71), the probability reads in the semiclassical limit

$$P(E) = P_{\text{sc}}(E) \left[ \Theta(E) - \frac{\hbar^2}{24} \omega(E) \omega(0) \delta'(E) - \hbar^2 \omega(0) J_2(0) \delta(E) + \mathcal{O}(\hbar^4) \right]. \quad (82)$$

Now, as a consequence of Eq. (30), we have

$$P_{\text{sc}}^{(\text{eq})}(E) = \frac{e^{-\beta E}}{Z} \rho_{\text{sc}}(E). \quad (83)$$

The equilibrium distribution function then takes the form

$$P_{\text{eq}}(E) = \frac{e^{-\beta E}}{\hbar Z} \left\{ \frac{\Theta(E)}{\omega(E)} - \hbar^2 \left[ (J_2 \Theta)'(E) + \frac{\omega(0)}{24} \delta'(E) \right] + \mathcal{O}(\hbar^4) \right\}. \quad (84)$$

Thus, to second order in  $\hbar$  equilibrium expectation values (33) are given by

$$\begin{aligned} \langle f(E) \rangle_{\text{eq}} = \frac{1}{\hbar Z} & \left\{ \int_0^\infty dE e^{-\beta E} \left[ \frac{1}{\omega(E)} - \hbar^2 J_2'(E) \right] f(E) \right. \\ & \left. + \frac{\hbar^2}{24} \omega(0) [f'(0) - \beta f(0)] - \hbar^2 J_2(0) f(0) + \mathcal{O}(\hbar^4) \right\}. \end{aligned} \quad (85)$$

Using this for  $f(E) \equiv 1$ , the partition function  $Z$  is found to read

$$\hbar Z = \hbar Z_{\text{cl}} - \hbar^2 \left[ \int_0^\infty dE J_2'(E) e^{-\beta E} + \frac{1}{24} \beta \omega(0) + J_2(0) \right] + \mathcal{O}(\hbar^4) \quad (86)$$

where

$$Z_{\text{cl}} = \frac{1}{\hbar} \int_0^\infty dE \frac{e^{-\beta E}}{\omega(E)}. \quad (87)$$

is the classical partition function. Of course, truncation of the expansion in terms of  $\hbar$  limits the range of temperatures to  $k_B T \gg \hbar \omega_0$  as is readily seen from Eqs. (84)-(86).

#### D. Semiclassical expansion of the transition rate

To expand the transition rate in the semiclassical limit we define

$$W_l(E) := W_{N_{\text{sc}}(E)+l, N_{\text{sc}}(E)} \quad (88)$$

which reads in view of Eqs. (26) and (67)

$$W_l(E) = \frac{1}{\hbar^2} B_l(E) D(\hbar A_l(E)). \quad (89)$$

The semiclassical expansion is given by

$$W_l(E) = \frac{1}{\hbar^2} W_l^{(0)}(E) + \frac{1}{\hbar} W_l^{(1)}(E) + W_l^{(2)}(E) + \hbar W_l^{(3)}(E) + \dots \quad (90)$$

Introducing the cosine moment of the damping kernel



$$\gamma_c(z) = \text{Re } \hat{\gamma}(iz), \quad (91)$$

the coefficients of the expansion (90) take the form

$$\begin{aligned} W_l^{(0)} &= \frac{2M}{\beta} B_l^{(0)} \gamma_c, \\ W_l^{(1)} &= \frac{lM\omega}{\beta} \left[ \left( -\beta B_l^{(0)} + [B_l^{(0)}]' \right) \gamma_c + |l|\omega' B_l^{(0)} \gamma_c' \right], \\ W_l^{(2)} &= \frac{M}{12\beta} \left[ \left( l^2 \{ -6\beta\omega\omega' + 2\beta^2\omega^2 \} B_l^{(0)} - 6\beta l^2\omega^2 [B_l^{(0)}]' + 12B_l^{(2)} \right) \gamma_c \right. \\ &\quad + \left( \{ |l|^3 [4\omega^2\omega'' + 4\omega(\omega')^2 - 6\beta\omega^2\omega'] + 24|l|\omega^2 J_2' \} B_l^{(0)} + 6|l|^3\omega^2\omega' [B_l^{(0)}]' \right) \gamma_c' \\ &\quad \left. + 3l^4\omega^2(\omega')^2 B_l^{(0)} \gamma_c'' \right], \\ W_l^{(3)} &= \frac{lM\omega}{24\beta} \left[ \left( \{ l^2 [-4\beta(\omega')^2 - 4\beta\omega\omega'' + 4\beta^2\omega\omega'] - 24\beta\omega J_2' \} B_l^{(0)} \right. \right. \\ &\quad + \{ l^2 [-2\omega\omega'' - 2(\omega')^2 - 6\beta\omega\omega' + 2\beta^2\omega^2] + 24\omega J_2' \} [B_l^{(0)}]' \\ &\quad - 6l^2\omega\omega' [B_l^{(0)}]'' - 2l^2\omega^2 [B_l^{(0)}]''' - 12\beta B_l^{(2)} + 12 [B_l^{(2)}]' \left. \right) \gamma_c \\ &\quad + \left( \{ |l|^3 [2\omega^2\omega''' + 2(\omega')^3 + 8\omega\omega'\omega'' - 10\beta\omega(\omega')^2 - 4\beta\omega^2\omega'' + 2\beta^2\omega^2\omega'] \right. \\ &\quad + |l| [72\omega\omega' J_2' + 24\omega^2 J_2'' - 24\beta\omega^2 J_2'] \left. \right) B_l^{(0)} \\ &\quad + \{ |l|^3 [4\omega(\omega')^2 + 4\omega^2\omega'' - 6\beta\omega^2\omega'] + 24|l|\omega^2 J_2' \} [B_l^{(0)}]' + 12|l|\omega' B_l^{(2)} \left. \right) \gamma_c' \\ &\quad + \left( \{ l^4 [4\omega(\omega')^3 + 4\omega^2\omega'\omega'' - 3\beta\omega^2(\omega')^2] + 24l^2\omega^2\omega' J_2' \} B_l^{(0)} + 3l^4\omega^2(\omega')^2 [B_l^{(0)}]' \right) \gamma_c'' \\ &\quad \left. + |l|^5\omega^2(\omega')^3 B_l^{(0)} \gamma_c''' \right], \end{aligned} \quad (92)$$

where  $\gamma_c^{(i)}(l\omega(E))$  was abbreviated by  $\gamma_c^{(i)}$  and the energy dependence was again suppressed.

## E. Semiclassical expansion of the master equation

We are now prepared to address the expansion of the master equation (37), which may be rewritten as

$$\dot{P}(E) = \sum_{n=0}^{\infty} \sum_{l=-n}^{\infty} [\delta(E - E_n - \hbar A_l(E_n)) - \delta(E - E_n)] W_l(E_n) p_n. \quad (93)$$

Using the relations

$$[\delta(E - E_n - \hbar A_l(E_n)) - \delta(E - E_n)] f(E_n) = \sum_{k=1}^{\infty} \left( \frac{\partial}{\partial E} \right)^k \frac{[-\hbar A_l(E)]^k}{k!} \delta(E - E_n) f(E) \quad (94)$$

and

$$\sum_{n=0}^{\infty} \sum_{\substack{l=-n \\ l \neq 0}}^{\infty} f(n, l) = \sum_{l=1}^{\infty} \left\{ \sum_{n=0}^{\infty} [f(n, l) + f(n, -l)] - \sum_{n=0}^{l-1} f(n, -l) \right\}, \quad (95)$$

we find from Eq. (93)

$$\dot{P}(E) = \sum_{k=1}^{\infty} \left( \frac{\partial}{\partial E} \right)^k \frac{(-\hbar)^k}{k!} \sum_{l=1}^{\infty} \left\{ [A_l(E)]^k W_l(E) + [A_{-l}(E)]^k W_{-l}(E) \right\} P(E) + P_B(E) \quad (96)$$

where

$$P_B(E) := - \sum_{k=1}^{\infty} \left( \frac{\partial}{\partial E} \right)^k \frac{(-\hbar)^k}{k!} \sum_{l=1}^{\infty} [A_{-l}(E)]^k W_{-l}(E) \sum_{n=0}^{l-1} \delta(E - E_n) p_n \quad (97)$$

is a boundary term which vanishes since

$$W_{-l}(E_n) \propto B_{-l}(E_n) = \langle n - l | q | n \rangle = 0 \quad \text{for } n \leq l - 1. \quad (98)$$

Despite the fact that the expansion (90) of  $W_l(E)$  starts with a term of order  $\hbar^{-2}$ , the series expansion in  $\hbar$  of the rhs of Eq. (96) does not contain terms of order  $\hbar^{-1}$  since they vanish due to the symmetry of  $\gamma_c(l\omega(E))$  and  $Q_l^{(0)}(E)$  in  $l$ . In leading order we then have

$$\dot{P}(E) = \mathcal{L}_0 P(E) \quad (99)$$

where

$$\mathcal{L}_0 = \frac{1}{\beta} \frac{\partial}{\partial E} e^{-\beta E} \Lambda^{(0)}(E) \frac{\partial}{\partial E} e^{\beta E} \frac{\omega(E)}{2\pi} \quad (100)$$

with  $\Lambda^{(0)}(E)$  defined in Eq. (19). Hence, we have recovered the Zwanzig energy diffusion equation (18).

The next order correction of order  $\hbar$  vanishes by symmetry. Thus, the leading quantum corrections are of order  $\hbar^2$ . Inserting the expansions provided in the previous subsections, one obtains a large number of terms that, after some manipulations, may be combined to give

$$\dot{P}(E) = (\mathcal{L}_0 + \hbar^2 \mathcal{L}_2)P(E) \quad (101)$$

where

$$\begin{aligned} \mathcal{L}_2 = & \frac{1}{\beta} \frac{\partial}{\partial E} e^{-\beta E} \left[ \Lambda^{(2)}(E) + \Phi(E) + \frac{\partial}{\partial E} \chi(E) e^{\beta E} \frac{\partial}{\partial E} e^{-\beta E} \right] \frac{\partial}{\partial E} e^{\beta E} \frac{\omega(E)}{2\pi} \\ & + \mathcal{L}_0 J'_2(E) \omega(E). \end{aligned} \quad (102)$$

We also have introduced the functions

$$\chi = \frac{\pi M \omega^3}{3} \sum_{l=1}^{\infty} l^4 B_l^{(0)} \gamma_c, \quad (103)$$

$$\Lambda^{(2)} = 2\pi M \omega \sum_{l=1}^{\infty} \left\{ l^2 \left[ 2\omega J'_2 B_l^{(0)} + B_l^{(2)} \right] \gamma_c + 2l^3 \omega^2 J'_2 B_l^{(0)} \gamma'_c \right\}, \quad (104)$$

and

$$\Phi = \frac{\pi M \omega}{18} \sum_{l=1}^{\infty} \left( 3l^4 \left\{ (\omega^2)'' B_l^{(0)} - 2\omega^2 [B_l^{(0)}]'' \right\} \gamma_c + 2l^5 \omega [(\omega^3)' B_l^{(0)}]' \gamma'_c + 3l^6 \omega^2 (\omega')^2 B_l^{(0)} \gamma''_c \right). \quad (105)$$

Note that the function (104) combines with Eq. (19) to the generalized energy relaxation coefficient

$$\Lambda(E) = 4\pi M \Omega(E) \sum_{l=1}^{\infty} l^2 B_l(E) \gamma_c(l\Omega(E)) = \Lambda^{(0)}(E) + \hbar^2 \Lambda^{(2)}(E) + \mathcal{O}(\hbar^3). \quad (106)$$

#### IV. GENERALIZED ENERGY DIFFUSION EQUATION

The results of the previous section can be summarized as follows. The generalized energy diffusion equation containing the leading quantum corrections can be written in the form

$$\begin{aligned} \dot{P}(E) = & \frac{1}{\beta} \frac{\partial}{\partial E} \left\{ e^{-\beta E} \left[ \Lambda(E) + \hbar^2 \Phi(E) \right. \right. \\ & \left. \left. + \hbar^2 \frac{\partial}{\partial E} \chi(E) e^{\beta E} \frac{\partial}{\partial E} e^{-\beta E} \right] \frac{\partial}{\partial E} e^{\beta E} \frac{\Omega(E)}{2\pi} \right\} P(E) = \mathcal{L}P(E) \end{aligned} \quad (107)$$

Here  $\Omega(E)$  is a generalized oscillation frequency containing quantum corrections as defined in Eq. (49).  $\Lambda(E)$  is given in Eq. (106) and contains the obvious quantum corrections to

the classical energy relaxation coefficient. The functions  $\Phi(E)$  and  $\chi(E)$  were introduced in Eqs. (105) and (103), respectively. Apart from the classical quantities  $\omega(E)$ ,  $Q_l^{(0)}(E)$ , and  $\hat{\gamma}(z)$  that are ingredients of the classical Zwanzig equation, one merely needs to calculate  $J_2(E)$  given in Eq. (46) and the second order quantum correction  $Q_l^{(2)}(E)$  of the dipole matrix element given in Eq. (63) in order to determine the generalized Fokker-Planck operator in Eq. (107) explicitly. Since one can show that the equilibrium solution (84) is a stationary solution of Eq. (107), the only non-trivial quantum correction that survives in equilibrium is seen to be the quantity  $J_2(0)$ .

In the case of an Ohmic bath, i.e.  $\gamma_c(\omega) = \gamma$ , the coefficients become particularly simple. Given the functions  $\omega$ ,  $J_2$ , and  $B_l^{(0/2)}$ , all quantities entering Eq. (107) can be expressed in terms of three sums

$$\begin{aligned}\lambda^{(i)} &= 4\pi M\gamma \sum_{l=1}^{\infty} l^2 B_l^{(i)}, \quad (i = 0, 2), \\ \phi &= 4\pi M\gamma \sum_{l=1}^{\infty} l^4 B_l^{(0)}.\end{aligned}\tag{108}$$

Then

$$\begin{aligned}\Omega &= \omega + \hbar^2 \omega^2 J_2', \\ \chi &= \frac{1}{12} \omega^3 \phi, \\ \Phi &= \frac{\omega}{24} [(\omega^2)'' \phi - 2\omega^2 \phi''], \\ \Lambda &= \omega \lambda^{(0)} + \hbar^2 \left[ \omega^2 J_2' \lambda^{(0)} + \frac{1}{2} \omega \lambda^{(2)} \right].\end{aligned}\tag{109}$$

### A. Harmonic oscillator

The simplest model for a molecular system, which already exhibits many of the characteristic features of VER, is the harmonic oscillator potential:

$$V(q) = \frac{1}{2} M \omega_0^2 q^2.\tag{110}$$

For the potential (110) one obtains

$$\begin{aligned}
\omega(E) &= \omega_0, \\
J_2(E) &= 0, \\
Q_{\pm 1}^{(0)}(E) &= \sqrt{\frac{E}{2M\omega_0^2}},
\end{aligned} \tag{111}$$

and the squared matrix elements read

$$B_{\pm 1}(E) = \frac{1}{2M\omega_0^2} \left( E \pm \hbar \frac{\omega_0}{2} \right). \tag{112}$$

Special to the case of the harmonic oscillator is the fact that  $B_l(E)$  vanishes for  $l \neq \pm 1$ .

The transition rates are

$$W_{\pm 1}(E) = \pm \frac{\gamma_c}{\hbar\omega_0} \bar{n}(\pm \hbar\omega_0) \left( E \pm \frac{\hbar\omega_0}{2} \right) \tag{113}$$

where  $\bar{n}(E)$  was introduced in Eq. (28). The Pauli master equation reads in terms of the probability  $P(E)$

$$\begin{aligned}
\dot{P}(E) &= \frac{\gamma_c}{\hbar\omega_0} \left[ \bar{n}(\hbar\omega_0) \left( e^{-\hbar\omega_0 \frac{\partial}{\partial E}} - 1 \right) \left( E + \frac{\hbar\omega_0}{2} \right) \right. \\
&\quad \left. - \bar{n}(-\hbar\omega_0) \left( e^{\hbar\omega_0 \frac{\partial}{\partial E}} - 1 \right) \left( E - \frac{\hbar\omega_0}{2} \right) \right] P(E).
\end{aligned} \tag{114}$$

For the energy relaxation coefficient (19) and the coefficients (103)-(105) one finds

$$\begin{aligned}
\Lambda^{(0)}(E) &= \frac{\gamma_c E}{\omega_0}, \\
\chi(E) &= \frac{\gamma_c \omega_0 E}{12}, \\
\Lambda^{(2)}(E) &= 0, \\
\Phi(E) &= 0,
\end{aligned} \tag{115}$$

so that the generalized energy diffusion equation (107) takes the form

$$\begin{aligned}
\dot{P}(E) &= \frac{\gamma_c}{\beta} \frac{\partial}{\partial E} \left( E [\beta P(E) + P'(E)] \right. \\
&\quad \left. + \frac{\hbar^2 \omega_0^2}{12} \left\{ [\beta^2 P'(E) + 2\beta P''(E) + P^{(3)}(E)] E + \beta P'(E) + P''(E) \right\} \right).
\end{aligned} \tag{116}$$

This equation can be solved in terms of the Fourier transform

$$\tilde{P}(u) = \int_{-\infty}^{\infty} dE e^{iuE} P(E). \quad (117)$$

Despite the fact that  $P(E) = 0$  for  $E < 0$ , the integral runs over all energies to collect possible contributions of delta functions at  $E = 0$ . The Fourier transform of Eq. (116) takes the form

$$\begin{aligned} \tilde{P}(u) = \frac{i\gamma_c}{\beta} u \left\{ \tilde{P}(u) + i(\beta - iu)\tilde{P}'(u) \right. \\ \left. + \frac{\hbar^2 \omega_0^2}{12} (\beta - iu) \left[ (\beta - 2iu)\tilde{P}(u) + u(\beta - iu)\tilde{P}'(u) \right] \right\}. \end{aligned} \quad (118)$$

This first order partial differential equation can be solved by the method of characteristics. The general solution is given by

$$\begin{aligned} \tilde{P}(u) = \frac{\beta}{\beta - i(1 - e^{-\gamma_c t})u} \tilde{P}_0 \left( \frac{-i\beta e^{-\gamma_c t} u}{\beta - i(1 - e^{-\gamma_c t})u} \right) \\ + i\hbar^2 \frac{\beta \omega_0^2 (1 - e^{-\gamma_c t}) u (\beta - iu)}{12 [\beta - i(1 - e^{-\gamma_c t})u]^3} \left\{ \frac{-i\beta^2 (\beta - iu) e^{-\gamma_c t} u}{\beta - i(1 - e^{-\gamma_c t})u} \tilde{P}'_0 \left( \frac{-i\beta e^{-\gamma_c t} u}{\beta - i(1 - e^{-\gamma_c t})u} \right) \right. \\ \left. + \frac{1}{2} \left[ -(1 - e^{-\gamma_c t})u^2 - i\beta(3 + e^{-\gamma_c t})u + 2\beta^2 \right] \tilde{P}_0 \left( \frac{-i\beta e^{-\gamma_c t} u}{\beta - i(1 - e^{-\gamma_c t})u} \right) \right\} \end{aligned} \quad (119)$$

where  $\tilde{P}_0(u)$  is the initial distribution. For  $t \rightarrow \infty$  this solution tends to

$$\tilde{P}(u) = \frac{\beta}{\beta - iu} - \frac{\hbar^2 \omega_0^2 \beta}{24} \left( \beta - iu - \frac{\beta^2}{\beta - iu} \right) \quad (120)$$

where we have used  $\tilde{P}_0(0) = 1$  which is just the normalization condition. The inverse Fourier transform of this stationary probability gives

$$P(E) = \Theta(E) \beta \left( 1 + \frac{\hbar^2 \omega_0^2 \beta^2}{24} \right) e^{-\beta E} - \frac{\hbar^2 \omega_0^2 \beta}{24} (\beta \delta(E) + \delta'(E)). \quad (121)$$

This result coincides with Eq. (84) if one inserts the quantum mechanical partition function  $Z = 1/[2 \sinh(\hbar \omega_0 \beta / 2)]$  and expands up to second order in  $\hbar$ .

As a specific example consider a system with given initial energy  $E_0$ , i.e.

$$P_0(E) = \delta(E - E_0). \quad (122)$$

Then moments are readily calculated from Eq. (119) using

$$\tilde{P}(u) = 1 + iu\langle E(t) \rangle - \frac{u^2}{2}\langle E^2(t) \rangle + \dots \quad (123)$$

This way the expectation value is found to read

$$\langle E(t) \rangle = E_0 e^{-\gamma_c t} + \left( \frac{1}{\beta} + \frac{\hbar^2 \omega_0^2 \beta}{12} \right) (1 - e^{-\gamma_c t}) \quad (124)$$

and the second moment obeys

$$\begin{aligned} \langle E^2(t) \rangle = & \frac{1}{\beta^2} [(\beta^2 E_0^2 - 4\beta E_0 + 2)e^{-2\gamma_c t} + 4(\beta E_0 - 1)e^{-\gamma_c t} + 2] \\ & + \frac{\hbar^2 \omega_0^2}{12} [(-4\beta E_0 + 7)e^{-2\gamma_c t} + 4(\beta E_0 - 2)e^{-\gamma_c t} + 1]. \end{aligned} \quad (125)$$

From Eq. (124) one finds that for the case of linear dissipation considered here the energy relaxation time

$$T_1 = \frac{1}{\gamma_c} \quad (126)$$

is not modified by quantum effects in accordance with the findings by Bader and Berne<sup>7</sup>.

## B. Morse oscillator

The fact that the relaxation time is unaffected by quantum effects is of course a special feature of the simple harmonic potential (110). As an example of a more realistic model for VER we consider a damped Morse oscillator. This system plays an important role in the modeling of, e.g., diatomic molecular systems. The Hamiltonian of the Morse oscillator reads

$$H = \frac{P^2}{2M} + D_0 [1 - e^{-\kappa(r-r_0)}]^2 \quad (127)$$

where  $D_0$  is the dissociation energy,  $r_0$  the nuclear distance at equilibrium, and  $\kappa^{-1}$  the range of the molecular potential. Here, the  $P = Mdr/d\tau$  is the classical momentum. In terms of the scaled variables  $q = \kappa(r - r_0)$ ,  $p = P/\sqrt{2D_0M}$ ,  $t = \tau\kappa\sqrt{2D_0/M}$  the Hamiltonian takes the form

$$H(p, q) = \frac{p^2}{2} + V(q) \quad (128)$$

where

$$V(q) = \frac{1}{2}(1 - e^{-q})^2. \quad (129)$$

Note that now  $\hbar$  is dimensionless and stands for  $\hbar\kappa/\sqrt{2D_0M}$ . The classical trajectory for a bound particle with energy  $E < 1/2$  is found by solving

$$2E - 1 = \dot{q}^2 + e^{-2q} - 2e^{-q} \quad (130)$$

with the result

$$q(E, t) = \ln \left[ \frac{1 + \sqrt{2E} \cos(t\sqrt{1-2E})}{1 - 2E} \right]. \quad (131)$$

Here we have assumed that the particle is at a turning point at  $t = 0$ . From this result it is seen that the energy dependent frequency is given by

$$\omega(E) = \sqrt{1 - 2E}. \quad (132)$$

To find the Fourier coefficients we write the trajectory in the form

$$q(E, t) = \ln \left[ \frac{1 + \sqrt{1 - 2E}}{2(1 - 2E)} \right] + \ln[1 - z_2(E)e^{i\omega(E)t}] + \ln[1 - z_2(E)e^{-i\omega(E)t}] \quad (133)$$

where

$$z_{1/2}(E) = -\frac{1 \pm \sqrt{1 - 2E}}{\sqrt{2E}}. \quad (134)$$

An expansion of the logarithms gives for  $l \neq 0$  the Fourier coefficients

$$Q_l(E) = -\frac{[z_2(E)]^{|l|}}{|l|} = -\frac{(-1)^{|l|}}{|l|} \left[ \frac{1 - \omega(E)}{1 + \omega(E)} \right]^{|l|/2}. \quad (135)$$

Further, the action variable  $J_0(E)$  is obtained by integration of Eq. (47) as

$$J_0(E) = \int_0^E \frac{dE'}{\omega(E')} = 1 - \sqrt{1 - 2E}, \quad (136)$$

and the second eikonal  $S_2(E, q)$  can also be integrated exactly yielding



$$S_2(E, q) = \frac{-6E + 8E^2 + 6e^{-2q}E + 1 - 3e^{-q} + 3e^{-2q} - e^{-3q}}{48E(2E - 1 + 2e^{-q} - e^{-2q})^{3/2}}. \quad (137)$$

Therefore, according to Eq. (46) we have  $J_2(E) = 0$ . Similarly, one finds

$$C^{(2)}(E) = 0. \quad (138)$$

The contour integral in Eq. (63) may be evaluated conveniently by means of the substitutions

$$\begin{aligned} e^{i\omega(E)t} &\rightarrow z, \\ dt &\rightarrow \frac{dz}{iz\omega(E)}, \\ p(E, t) &\rightarrow \frac{i(z^2 - 1)(z_2^2 - 1)z_2}{(zz_2 - 1)(z_2 - z)(z_2^2 + 1)}, \\ \exp[-q(E, t)] &\rightarrow \frac{(z_2^2 - 1)^2 z}{(zz_2 - 1)(z_2 - z)(z_2^2 + 1)}. \end{aligned} \quad (139)$$

One then finds

$$Q_l^{(2)}(E) = Q_l^{(0)}(E)|l| \frac{3\omega^2(E)|l|^3 - 8\omega^3(E)l^2 - 12|l|E^2 + 2\omega^3(E)}{96E^2\omega^2(E)}, \quad (140)$$

which gives for the squared matrix element

$$B_l^{(2)}(E) = [Q_l^{(0)}]^2(E) \frac{\omega^3(E)(1 - 4l^2) + 3|l|(l^2\omega^2(E) - 2E^2)}{12|l|\omega^2(E)E^2}. \quad (141)$$

Restricting ourselves to the Ohmic case  $\gamma_c(\omega) = \gamma$ , one only needs to calculate the functions (108) which read

$$\begin{aligned} \lambda^{(0)}(E) &= 2\pi\gamma \left[ (1 - 2E)^{-1/2} - 1 \right], \\ \lambda^{(2)}(E) &= 2\pi\gamma(E + 2)(1 - 2E)^{-3/2}, \end{aligned} \quad (142)$$

$$\phi(E) = 2\pi\gamma E(1 - 2E)^{-3/2}. \quad (143)$$

Using Eq. (109) we then find

$$\begin{aligned} \chi(E) &= 2\pi\gamma \frac{E}{12}, \\ \Phi(E) &= -2\pi\gamma \frac{E + 2}{4(1 - 2E)^2}, \\ \Lambda^{(2)}(E) &= 2\pi\gamma \frac{E + 2}{4(1 - 2E)^2}. \end{aligned} \quad (144)$$

Thus, the generalized energy diffusion equation takes the form

$$\dot{P}(E) = \frac{\gamma}{\beta} \frac{\partial}{\partial E} e^{-\beta E} \left[ J_0(E) + \frac{\hbar^2}{12} \frac{\partial}{\partial E} E e^{\beta E} \frac{\partial}{\partial E} e^{-\beta E} \right] \frac{\partial}{\partial E} e^{\beta E} \omega(E) P(E). \quad (145)$$

We recall that all quantities are dimensionless, in particular the dimensionless energy  $E$  is measured in units of  $2D_0$  and  $\beta = 2D_0/k_B T$ .

Let us now investigate how an initial probability

$$P_0(E) = \delta(E - E_0) \quad (146)$$

evolves for short times. Using

$$\left. \frac{\partial}{\partial t} \langle f(E(t)) \rangle \right|_{t=0} = \int dE \mathcal{L} P_0(E) f(E) \quad (147)$$

one finds for the initial change of the energy expectation value and the second moment

$$\begin{aligned} \left. \frac{\partial}{\partial t} \langle E(t) \rangle \right|_{t=0} &= -\gamma \left[ \omega J_0 - \left( \frac{1}{\beta} + \frac{1}{12} \hbar^2 \beta \omega \right) \right], \\ \left. \frac{\partial}{\partial t} \langle E^2(t) \rangle \right|_{t=0} &= -2\gamma \left[ \omega J_0 - \left( \frac{\omega J_0 + E_0}{\beta} + \frac{1}{12} \hbar^2 \omega \gamma (2\beta E_0 - 3) \right) \right]. \end{aligned} \quad (148)$$

It is useful to discuss this result in terms of the relaxation rate  $R(E_0)$  defined by

$$\left. \frac{\partial}{\partial t} \langle E(t) \rangle \right|_{t=0} = -R(E_0) E_0. \quad (149)$$

From Eq. (148) one sees that quantum corrections lower the relaxation rate since the mean thermal energy is raised by zero point motion. Usually this effect is accounted for by the definition of the relaxation time  $T_1$  according to

$$\frac{\partial}{\partial t} \langle E(t) \rangle = -\frac{1}{T_1} [\langle E(t) \rangle - \langle E \rangle_{\text{eq}}]. \quad (150)$$

Contrary to the harmonic case  $\omega J_0 \neq E$ , and the energy relaxation is non-exponential for high energies where anharmonicities are important. The usual concept of a relaxation time is thus no longer strictly valid. Eq. (150) may, however, serve in connection with Eq. (148) to define an initial relaxation rate  $1/T_1$ . For the classical relaxation time one then finds for  $\beta \gg 1$  (that is the potential is almost harmonic for thermal energies)

$$T_1^{\text{cl}} = \frac{E_0 - 1/\beta}{\gamma(\omega J_0 - 1/\beta)}, \quad (151)$$

from where it is readily seen that the classical relaxation time increases as the initial energy increases, consistent with the fact that the period increases with energy. The semiclassical corrections to the relaxation time are then found by using Eqs. (85) and (86). The leading order correction to Eq. (151) is found to read

$$\frac{T_1^{\text{sc}}}{T_1^{\text{cl}}} = 1 - \frac{1}{12} \hbar^2 \beta \left( \frac{1}{E_0} - \frac{1}{J_0} \right) \quad (152)$$

from where the classical and harmonic limits are readily recovered by setting  $\hbar = 0$  and  $J_0(E_0) = E_0$ , respectively. With the rates defined in this way, we now find an acceleration of the relaxation process by quantum fluctuations.

To investigate the quality of the semiclassical energy diffusion equation in some detail, we compare with results of the full master equation. Since for the Morse potential exact dipole matrix elements are available<sup>15</sup>, the initial energy relaxation rate may be calculated using

$$\frac{\partial}{\partial t} \langle E(t) \rangle = \sum_{n,m=0}^{\infty} p_m(t) W_{mn} (E_n - E_m) \quad (153)$$

which is a consequence of the master equation (22). To compare this with the approximation (148), one has to consider an initial distribution

$$p_n(0) = \delta_{n,n_0}. \quad (154)$$

For Ohmic damping we then have

$$\left. \frac{\partial}{\partial t} \langle E(t) \rangle \right|_{t=0} = -R(n_0) E_0 = 2\gamma_c \sum_{l=-n_0}^{N_{\text{max}}-n_0} \frac{B_l(E_0) [A_l(E_0)]^2}{e^{\hbar\beta A_l(E_0)} - 1} \quad (155)$$

where  $E_0 = E_{n_0}$ ,

$$A_l(E) = l\omega(E) - \frac{l^2}{2} \hbar \quad (156)$$

and  $B_l(E)$  is given by<sup>15</sup>

$$B_l(E) = [Q_l(E)]^2 = \frac{\left(\frac{\omega(E)}{\hbar} - l\right) \Gamma\left(\frac{1}{\hbar} + \frac{1}{2} + \frac{\omega(E)}{\hbar}\right) \Gamma\left(\frac{1}{\hbar} + \frac{1}{2} - \frac{\omega(E)}{\hbar}\right)}{\left(\frac{\omega(E)}{\hbar} - \frac{l}{2}\right) \Gamma\left(\frac{1}{\hbar} + \frac{1}{2} + \frac{\omega(E)}{\hbar} - l\right) \Gamma\left(\frac{1}{\hbar} + \frac{1}{2} - \frac{\omega(E)}{\hbar} + l\right)}. \quad (157)$$

Figure 1 compares the relaxation rates  $R(n_0)$  for the parameters  $\hbar = 0.0943$ ,  $\beta = 20$  (ten bound states) and  $\hbar = 0.0198$ ,  $\beta = 100$  (50 bound states). Since  $N_{\text{sc}}(\langle E \rangle_{\text{eq}}) = 0.27$  and  $0.17$ , respectively, in equilibrium only the ground state is populated substantially. Hence,  $R(n)$  is negative for  $n = 0$  only. The figure shows that for higher states the classical rates agree well with the quantum results. For low-lying states, however, while the classical approximation fails the semiclassical rates are still in good agreement with the master equation prediction.

## V. CONCLUSIONS

We have given a systematic semiclassical theory of vibrational energy relaxation based on the quantum master equation. Specifically, we have studied a model leading to a generalized Langevin equation in the classical limit, which is the basis of much of the earlier work. An expansion in powers of  $\hbar$  (more specifically, in powers of  $\hbar\omega_0/k_B T$ , where  $\hbar\omega_0/2$  is the vibrational zero point energy) was shown to yield the Zwanzig energy diffusion equation and quantum corrections thereof. For a harmonic potential, the energy relaxation time is not affected by quantum fluctuations while it can be reduced for nonlinear potentials. For the Morse potential the improved energy diffusion equation was shown to incorporate the main quantum effects.

## ACKNOWLEDGMENTS

The authors would like to thank D. Richards for helpful correspondence and acknowledge useful discussions with F. J. Weiper and C. A. Stafford. Financial support was provided by the Sonderforschungsbereich 276 of the Deutsche Forschungsgemeinschaft (DFG, Bonn).

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# FIGURES

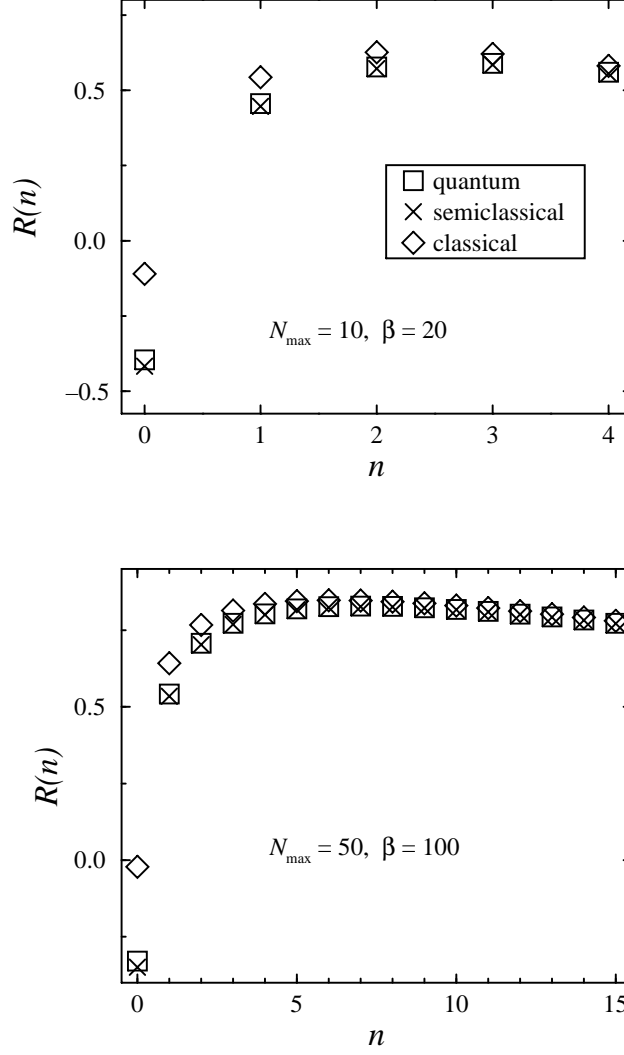


FIG. 1. Comparison of energy relaxation rates  $R(n)$  for various initial states  $n$  based on classical, semiclassical and quantum theories for the Morse potential and two sets of parameters.  $R(n)$  is given in units of  $\gamma_c$ . Ground state rates are negative since in equilibrium also higher vibrational levels are populated.